

DEVELOPING THIN FILM COMPOSITE MEMBRANES FOR ENGINEERED OSMOSIS PROCESSES

by

Soleyman Sahebi

A Thesis submitted in fulfilment for the degree of

Doctoral of Philosophy



**School of civil and Environmental Engineering
Faculty of Engineering and Information Technology
University of Technology, Sydney (UTS),
New South Wales, Australia**

Jun 2015

Certificate of Authorship

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Soleyman Sahebi

Signature of Student:



Date: 28-06-2015

ACKNOWLEDGEMENTS

I wish to express my heartfelt gratitude for my mother Mrs Sara for whom my success and progress matter the most. Her encouragement and inspiration gave me strength throughout my entire life. She was mother and father for me and my siblings from the very moment of our childhood since my father passed away early. Nothing is enough to appreciate her young life she spent for me, my brother and sister. Then I would like to dedicate this thesis that I achieved through a great challenge to my dear mom. Without her sacrifices, I never could have reached this stage. I also dedicate my thesis to my father who passed away very early but through his hard work and wise planning, our family managed to overcome all challenges and financial hardship years after his passing.

This dissertation would not have been possible without the support and encouragement of my principal supervisor Dr. Ho Kyong Shon. I would like to express my deepest gratitude and appreciation to him. I would like also to thank my co-supervisor Dr. Sherub Phuntsho for his kind support and his wisdom during my study at UTS. I also would like to express my sincere appreciation to Prof. Chung Tai-Shung (Neal) who give me a training opportunity into his fascinating membrane research group and Dr Han Gang who worked with me during the time in the National University of Singapore (NUS). I have learned and benefited a lot from the training workshop and without this opportunity this thesis would not be possible.

I also would like to thank my friends and research group members at UTS who made this journey memorable. I want to thank Lura Chekli, Fouze Lotfi, Ibrahim El Saliby, Tahir Majeed, Jung Eun Kim, Yun Chul Woo, Myoung Jun Park and I also appreciate Dr. Leonard D. Tijning for his kind help during my study. I also thank my

elder brother Mr Saeed Sahebi and dear friend Dr. Diako Ebrahimi for their support and encouragement during my thesis when I faced very hard, stressful and challenging moments. Their advice gave me the light and encouragement to maintain the momentum.

Finally, I thank my beloved fiancé Nasim for the pain she has had to endure during my absence and cope with this condition in order to support my study while she had an internship and was passing through a difficult period of her study. I would like also to thank Nasim's family, especially her mother Mrs. Ziba Hesami who has been like a loving mother and Mr Salimiaghdam, who been as a precious father to me. I also want to thank my brother in-law Dr. Chia Salimiaghdam for his support during the time I was away and busy with this study.

Last but not least, I would like to thank the University of Technology, Sydney for offering me APA scholarships for my PhD studies at UTS and later on NCEDA scholarship by the National Centre of Excellence in Desalination Australia.

TABLE OF CONTENTS

Certificate of Authorship	2
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS.....	v
Journal Articles Published	ix
Conference papers and presentations.....	x
ABSTRACT	xi
LIST OF ABBREVIATIONS.....	xiv
LIST OF SYMBOLS	xv
LIST OF FIGURES.....	xvi
LIST OF TABLES.....	xxiii
Chapter 1	1
INTRODUCTION	1
1.1 Background.....	2
1.2 Research Motivation.....	4
1.3 Objectives and Scope of the Study	5
1.4 Structure Outline of the Thesis.....	7
Chapter 2	8
LITERATURE REVIEW	8
2.1 Introduction	9
2.2 Current and emerging technologies for global water crises	9
2.3 Forward osmosis (FO)	12
2.3.1 Pressure Assisted Osmosis (PAO)	15
2.3.2 PAO for energy savings in desalination units, oil and gas wastewater treatment.....	17
2.3.3 Pressure Retarded Osmosis (PRO).....	20
2.4 Hybrid FO applications.....	22
2.4.1 Hybrid RO-FO system	23
2.4.2 Hybrid PRO-MD system	25
2.5 FO challenges	28
2.5.1 Draw solution.....	28
2.5.2 Membrane.....	31
2.5.3 Fluid management	38

2.6	Membrane for engineered osmosis	39
2.6.1	Polymeric membranes	40
2.7	Engineering principles for the design of polymeric membranes.....	45
2.7.1	Phase inversion induced asymmetric membranes.....	46
2.8	Forward osmosis membrane fabrication methods.....	49
2.8.1	Phase inversion membranes.....	50
2.8.2	Composite membranes	53
2.8.3	Inorganic membranes.....	61
2.9	Custom designs of flat sheet FO membranes.....	64
2.9.1	Selective rejection layer.....	65
2.9.2	Support polymeric layer.....	68
2.9.3	Support backing fabric	73
2.10	Important factors in fabricating TFC FO membrane.....	78
2.10.1	Membrane wrinkling, creasing and defect points.....	78
2.10.2	Membrane pore size in support layer	81
2.10.3	Membrane pore size in skin layer.....	83
2.11	Concluding remarks and recommendations.....	86
Chapter 3		88
MATERIALS AND METHODS		88
3.1	Introduction	89
3.2	Experimental Materials	89
3.2.1	Membranes fabrication materials	89
3.2.2	Chemicals used as draw and feed solution	90
3.2.3	Membrane fabrication procedure	91
3.3	Membrane characterizations	93
3.3.1	Basic characterisation	93
3.3.2	Field Emission Scanning Electron Microscope (FESEM)	93
3.4	Forward osmosis (FO) and pressure assisted osmosis (PAO) test	94
3.4.1	FO lab scale set up and performance tests.....	94
3.4.2	PAO lab scale set up and performance tests	96
3.4.3	Water contact angle.....	97
3.4.4	Membrane porosity	98
3.4.5	Mechanical strength	99
3.5	Measurement and data analysis	100

3.5.1	Pure water permeability	100
3.5.2	Salt rejection and salt permeability tests	100
3.5.3	Measurement of the reverse solute flux.....	101
3.5.4	Determining membrane structural parameter	101
Chapter 4	103
PRESSURE ASSISTED FERTILISER DRAWN OSMOSIS PROCESS TO ENHANCE FINAL DILUTION OF FERTILISER DRAW SOLUTION BEYOND OSMOTIC EQUILIBRIUM ..		103
4.1	Introduction	104
4.2	Classification of osmotic processes and modelling.....	108
4.3	Materials and Methods	114
4.3.1	Feed and draw solutions	114
4.3.2	Bench-scale pressure assisted osmosis (PAO) experimental setup and its operation	115
4.4	Results and discussion.....	117
4.4.1	Validating the pressure assisted osmosis (PAO) process.....	117
4.4.2	PAO process for the pressure assisted fertiliser drawn osmosis (PAFDO) desalination.....	124
4.4.3	Reverse draw solute diffusion and feed solute rejection in the PAO process	131
4.4.4	Understanding the significance and implications of the PAFDO process	134
4.5	Concluding remarks.....	139
Chapter 5	141
THIN FILM COMPOSITE FORWARD OSMOSIS MEMBRANE ON A SULPHONATED POLYETHERSULFONE SUBSTRATE		141
5.1	Introduction	142
5.2	Material and methods	145
5.2.1	Chemicals.....	145
5.2.2	Synthesis of SPES polymer	145
5.2.3	Fabrication of flat-sheet TFC FO membranes	147
5.2.4	Membrane characterizations.....	149
5.2.5	FO performance experiments.....	150
5.3	Results and discussion.....	152
5.3.1	Characteristic of membrane substrates	152
5.3.2	Characterization of TFC-FO membranes	157
5.3.3	Performance of TFC-FO membranes for FO process	160

5.4	Concluding remarks.....	165
Chapter 6	167
THIN-FILM COMPOSITE MEMBRANE SUPPORTED ON A COMPACTED WOVEN FABRIC MESH SUPPORT FOR PRESSURE ASSISTED OSMOSIS.....		167
6.1	Introduction.....	168
6.2	Materials and Methods	172
6.2.1	Chemicals and membrane materials.....	172
6.2.2	Synthesis of flat-sheet TFC PAO membranes.....	173
6.2.3	Membrane characterization.....	177
6.3	Results and discussion.....	181
6.3.1	Membrane substrate layer.....	181
6.3.2	Membrane rejection layer.....	195
6.3.3	PAO performance evaluation.....	201
6.4	Concluding remarks.....	210
Chapter 7	212
CONCLUSIONS AND RECOMMENDATIONS.....		212
7.1	Pressure assisted fertilizer drawn osmosis process	213
7.2	Thin film composite forward osmosis membrane	214
7.3	Thin film composite supported on woven fabric for pressure assisted osmosis 216	
7.4	Recommendations and future work.....	219
REFERENCES	221

Journal Articles Published

1. ***Sahebi, S.**, Phuntsho, S., Eun Kim, J., Hong, S., & Kyong Shon, H. (2015). Pressure assisted fertiliser drawn osmosis process to enhance final dilution of the fertiliser draw solution beyond osmotic equilibrium. *Journal of Membrane Science*, 481(0), 63-72.
2. *Phuntsho, S., **Sahebi, S.**, Majeed, T., Lotfi, F., Kim, J. E., & Shon, H. K. (2013). Assessing the major factors affecting the performances of forward osmosis and its implications on the desalination process. *Chemical Engineering Journal*, 231, 484-496.
3. *Majeed, T., **Sahebi, S.**, Lotfi, F., Kim, J. E., Phuntsho, S., Tijing, L. D., & Shon, H. K. (2014). Fertilizer-drawn forward osmosis for irrigation of tomatoes. *Desalination and Water Treatment*, 53(10), 2746-2759.
4. **Chae, S.-R., Noeiaghahi, T., Jang, H.-C., Sahebi, S., Jassby, D., Shon, H.-K., Park, J.-S. (2015). Effects of natural organic matter on separation of the hydroxylated fullerene nanoparticles by cross-flow ultrafiltration membranes from water. *Separation and Purification Technology*, 140(0), 61-68.
5. *Majeed, T., Phuntsho, S., **Sahebi, S.**, Kim, J. E., Yoon, J. K., Kim, K., & Shon, H. K. (2014). Influence of the process parameters on hollow fiber-forward osmosis membrane performances. *Desalination and Water Treatment*, 54(4-5), 817-828.
6. **Ahmadi, M., Ramavandi, B., & **Sahebi, S.** (2014). Efficient Degradation of a Biorecalcitrant Pollutant from Wastewater Using a Fluidized Catalyst-Bed Reactor. *Chemical Engineering Communications*, 202(8), 1118-1129.
7. **Ramavandi, B., Asgari, G., Faradmal, J., **Sahebi, S.**, & Roshani, B. (2014). Abatement of Cr (VI) from wastewater using a new adsorbent, cantaloupe peel: Taguchi L16 orthogonal array optimization. *Korean Journal of Chemical Engineering*, 31(12), 2207-2214.
8. **Asgari, G., Ramavandi, B., & **Sahebi, S.** (2013). Removal of a cationic dye from wastewater during purification by *Phoenix dactylifera*. *Desalination and Water Treatment*, 52(37-39), 7354-7365.
9. **Ramavandi, B., Jafarzadeh, M., & **Sahebi, S.** (2014). Removal of phenol from hyper-saline wastewater using Cu/Mg/Al-chitosan-H₂O₂ in a fluidized catalytic bed reactor. *Reaction Kinetics, Mechanisms and Catalysis*, 111(2), 605-620.

Conference papers and presentations

1. *Soleyman Sahebi, Ho Kyong Shon , **Sherub Phuntsho**, Fezeh Lotfi, Jung Eun Kim. Factors Affecting the Performances of Forward Osmosis Desalination Process.
Euro-membrane conference. Sep 23 – 27, 2012, London, UK.
2. **Chae, So-Ryong; Jang, Hee-Chan; Lee, Jieun; Noeiaghahi, Tahereh; **Sahebi, Soleyman**; Shon, Ho-Kyong; Kim, Jong-Oh and Wiesner, Mark R. Recovery of engineered nanomaterials by dead-end and cross-flow ultrafiltration membranes from water : Chemeca 2012: Quality of life through chemical engineering: 23-26 September 2012, Wellington, New Zealand
3. *Sherub Phuntsho, **Soleyman Sahebi**, Amit Chanan, Ho Kyong Shon.,” Pressure assisted osmosis: overcoming limitations of osmotic equilibrium in forward osmosis process”, IWA-WWC&E 2014 Portugal.
4. ***Soleyman Sahebi**, Ho Kyong Shon , Sherub Phuntsho, Major factors affecting performances of forward osmosis desalination, FEIT Showcase June 12, 2012, Faculty of Engineering & Information Technology, University of Technology Sydney (UTS), Sydney, Australia.

**Publications made during the PhD candidature including articles not entirely related to the Thesis. *Articles related to the Thesis.

ABSTRACT

The high demand for clean water resources has generated substantial research interest in terms of sustainable and low energy water purification technologies such as forward osmosis (FO). Compared to other membrane based technologies, the FO process is less energy intensive. However, there are challenges that need solutions to enable the FO to compete with other technologies for desalination. Suitable draw solution and a proper membrane are required to overcome the FO process challenges. Enormous effort has been expended to find a new material and better membrane design in order to develop a novel FO membrane that can meet high performance demands in relation to water flux, salt rejection and mechanical strength. This is of particular importance for the newly introduced concept of pressure assisted osmosis (PAO). The objectives of this dissertation are to understand the fundamentals of the FO and PAO as a basis for fabricating a suitable membrane for the FO and PAO process.

In the first part of the work, PAO and its potential application to overcome the limitations of osmotic equilibrium in the FO process is investigated. One of the practical applications of the FO process is desalination for irrigation purposes through the means of hybrid desalination units such as fertiliser drawn forward osmosis (FDFO). The utilisation of PAO in FDFO desalination is assessed. By integrating the PAO process into the FDFO desalination unit, water flux can be generated beyond the point of osmotic equilibrium. As a result, diluted fertilizer as DS in the FDFO unit can be applied for direct fertigation without the need for an additional post-treatment process such as nanofiltration to recover the fertiliser draw solution (DS). Integration of the PAO process has proved to be very effective in

generating extra water flux. This can serve to reduce the capital costs since no separate post-treatment process such as the NF is necessary.

In the second part of the work, a thin film composite membrane for the FO and PAO process is fabricated through Polyethersulfone as a polymer materials base. Phase inversion in the precipitation bath and membrane formation mechanism of these polymers, both with and without backing fabric support, is investigated. The membrane chemical properties and hydrophilicity have been found to play a key role in the mass transfer of water flux during the FO process. Therefore, attention has been directed at increasing the hydrophilicity of the membrane through blending sulphonated materials. It has been found that sulphonation not only affects the membrane performance but also the membrane structure and morphology. Through sulphonation, porosity and hydrophilicity of the substrate increases while the finger like structure disappears. This leads one to suppose that the high water flux does not have a direct relationship with the finger like membrane structure. Regardless of membrane morphology, substrate hydrophilicity is the key to achieving a high performance membrane. Sulphonation has been found to have a tremendous effect on the physical and chemical properties of the membrane. While sulphonation dramatically increases the hydrophilicity of the substrate, it decreases the membrane mechanical strength. Due to higher hydrophilicity and lower ICP as a result of blending the sulphonation polymer, a membrane with better performance in terms of water flux and selectivity has been developed for the FO process.

In the last part of the work, a special thin film composite (TFC) flat sheet membrane on a backing fabric is developed for the PAO application. The newly developed concept of PAO has introduced a hydraulic pressure to the feed side to overcome

osmotic equilibrium and the extraction of more water. Accordingly, under the PAO process, a membrane with considerable mechanical strength is required. A thin film composite membrane supported on woven mesh fabric is designed to specifically solve the problem by embedding a woven mesh fabric support. An earlier part of this study reveals that the mechanical stability and special physical properties of the support layer are critical for the PAO process.

LIST OF ABBREVIATIONS

AL-DS	:	Active layer – draw solution
AL-FS	:	Active layer - feed solution
AL	:	Active layer
BW	:	Brackish water
CA	:	Cellulose acetate
CTA	:	Cellulose triacetate
CP	:	Concentration polarization
DI	:	Deionized water
DS	:	Draw solution
ECP	:	External concentration polarization
FDFO	:	Fertilizer drawn forward osmosis
FO	:	Forward osmosis
FS	:	Feed solution
ICP	:	Internal concentration polarization
IP	:	Interfacial polymerization
LMH	:	L/m ² /h
MW	:	Molecular weight
NF	:	Nanofiltration
PA	:	Polyamide
PAI	:	Poly (amide-imide)
PAO	:	Pressure assisted osmosis
PBI	:	Polybenzimidazole
PES	:	Polyethersulfone
PRO	:	Pressure-retarded osmosis
PSf	:	Polysulfone
PWP	:	Pure water permeability
RO	:	Reverse osmosis
RSF	:	Reverse solute flux
SEM	:	Scanning electron microscope
SL	:	Support layer
SRSF	:	Specific reverse solute flux
SW	:	Sea water
TFC	:	Thin film composite
TFN	:	Thin film nanocomposite

LIST OF SYMBOLS

A	:	Water permeability coefficient ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$)
B	:	Salt permeability coefficient ($\text{m} \cdot \text{s}^{-1}$)
D/Ds	:	Diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
J_s	:	Solute flux ($\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)
J_w	:	Water flux ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)
k	:	Mass transfer coefficient
K	:	Solute diffusion resistance ($\text{s} \cdot \text{m}^{-1}$)
M	:	Molar concentration of the solution
Mw	:	Molecular weight ($\text{mol} \cdot \text{g}^{-1}$)
n	:	Van't Hoff factor
P	:	Applied hydraulic pressure (bar)
Re	:	Reynolds number
Sc	:	Schmidt number
Sh	:	Sherwood number
T	:	Absolute temperature (in K)
t	:	Thickness of the membrane (m)
Δt	:	Time interval (h)
ΔV	:	Volume change (L)
ΔP	:	Pressure change (bar)
π	:	Osmotic pressure (bar)
ϕ	:	Osmotic pressure coefficient
σ	:	Reflection coefficient,
ε	:	Porosity
β	:	van't Hoff coefficient
τ	:	Tortuosity

LIST OF FIGURES

Figure 2.1 Illustration of major desalination technologies with their relative contributions to worldwide capacity for desalination.....	12
Figure 2.2 Water flow and relationship between RO, PRO, FO and PAO for an ideal semi-permeable membrane. In FO, water diffuses to the more saline side of the membrane and ΔP is approximately zero. PAO is similar to FO but additional pressure is applied on the feed side. In PRO, positive pressure ($\Delta\pi > \Delta P$) occurs and as a result of water diffuses to the more saline liquid side. In RO, due to hydraulic pressure ($\Delta P > \Delta\pi$), water diffuses to the less saline side.	13
Figure 2.3 Schematic of FDFO desalination unit for fertigation using NF for DS recovery.....	18
Figure 2.4 (a) Schematic of oil and gas waste water treatment applying FO and PAO process, adapted with permission from (Coday et al. 2014) , and (b) Illustration of Oasays' membrane brine concentrator (MBC)....	20
Figure 2.5 Illustration of a PRO system with relevant dimension.....	21
Figure 2.6 Schematic of hybrid forward osmosis systems for desalination of seawater, wastewater treatment and energy production.....	23
Figure 2.7 Schematic of hybrid pressure retarded osmosis–membrane distillation system for power generation from low-grade heat.....	27
Figure 2.8 Energy conversion from salinity gradients by forward osmosis–electrokinetics.....	27
Figure 2.9 Water flux transport in the PRO and FO mode in FO process (Wang et al. 2010).....	36
Figure 2.10 Illustration of the principal types of membrane in terms of their structure..	43
Figure 2.11. Schematic for membrane modules.....	46
Figure 2.12 Ternary phase diagram of system with three component used in Loeb–Sourirajan membranes fabrication (Husain 2012).....	49

Figure 2.13 Schematic of Loeb–Sourirajan membrane casting machine used to fabricate RO and UF membranes (Miller et al. 1966).....	51
Figure 2.14 Schematic of CTA FO membrane from HTI on woven polyester mesh (Yip et al. 2010).....	53
Figure 2.15 Illustration of (a) TFC and (b) TFN membrane with nano particles on selective layer (Jeong et al. 2007), and TFN membrane with nano particles within support structure layer (Ma et al. 2013).....	60
Figure 2.16 Shows layer-by-layer assembly of poly (allylamine hydrochloride) (PAH) and poly(sodium 4-styrene-sulfonate) (PSS) membrane, PSS was used as the polyanion and PAH as the polycation (Saren et al. 2011).....	61
Figure 2.17 (a) Aquaporin based biomimetic membranes fabricated through interfacial polymerization (Tang et al. 2013), and (b) Comparison of permeability for polymeric membranes of FO, RO and EE-EO membrane to ABA and AqpZ-ABA with incorporated AqpZ biomimetic membrane (Kumar et al. 2007).....	63
Figure 2.18 SEM images of TFI FO membrane (a) top surface, and (b) membrane cross section (You et al. 2013).....	64
Figure 2.19 A typical hand casting knife for fabricating FO membrane by Paul N. Gardner Company, Inc.....	67
Figure 2.20 (a) Diagram shows ion transport through and modified and unmodified membranes (Zhou. et al. 2009), (b) poly(ethylene glycol)-modified nascent TFC membranes and surface grafted poly(ethylene glycol) chain to repulsion of macromolecule (Kang et al. 2007), (c) Polyamide TFC membranes functionalized with graphene oxide for fouling control (Perreault et al. 2013), and (d) amine functionalized MWCNTs in MPD solution reacting with TMC to form better selective thin layer (Amini. et al. 2013).....	69
Figure 2.21 Poly (phthalazinone ether sulfone ketone), PPESK reaction into sulfonated poly(phthalazinone ether sulfone ketone), SPPEsk.....	74
Figure 2.22 Schematic of FO membrane made of nanofiber.....	74
Figure 2.23 Schematic illustration of membrane formation from polymer solution	

with graphene oxide (GO) through phase inversion (Ganesh et al. 2013).....	75
Figure 2.24 (a) shows CTA FO membrane from HTI with woven polyester mesh, (b) CTA FO from HTI with non-woven backing fabric, (c) thin film composite FO membrane on a non-woven fabric from Woongjin, (d) thin film composite FO membrane on woven polyester mesh from University of Technology Sydney.....	77
Figure 2.25 (a) non woven backing fabric used in RO membrane, (b) polyester mesh woven backing fabric used in TFC-HTI FO membrane.....	78
Figure 2.26 Schematic of Nanocelluloses thin membrane film (a) and SEM image of Nanocelluloses fibre (b) (Klemm et al. 2006).	80
Figure 2.27 (a) Membrane fabrication RO-style, and (b) FO style. Modified figure from (Herron 2008).	82
Figure 2.28 (a) SEM images of CA membranes fabricated from acetone and 2-methyl-2,4-pentanediol. The evaporation time is different for four samples (Mark & Kroschwitz 1989), (b) SEM images of PSF membranes fabricated from a solution of NMP and different non solvent in the precipitation bath (Guillen et al. 2011).	84
Figure 2.29 Schematic diagram of the interfacial polymerization process.....	86
Figure 2.30 Illustration of polyamide-polysulfone layers for two type TFC membrane (Singh et al. 2006).	87
Figure 2.31 The effects of PSF substrate and chemistry in producing TFC membrane through MPD-TMC reaction (a) higher permeability and surface with relative roughness, (b) relatively impermeable and medium surface roughness, (c) the highest permeability and the highest roughness, and (d) the lowest permeability and medium surface roughness (Ghosh & Hoek 2009a).	87
Figure 3.1: Stainless steel film applicator and the glass plate.	94
Figure 3.2: Membrane frame which was used for the interfacial polymerization.....	96
Figure 3.3: High-resolution Schottky field emission scanning electron microscope (SEM Zeiss Supra 55 VP).....	97

Figure 3.4: Schematic of the lab-scale crossflow forward osmosis experimental setup.	99
Figure 3.5: Schematic of the lab-scale experimental setup for pressure assisted osmosis process.	100
Figure 3.6: Optical tensiometer using the sessile drop method to measure membrane contact angles.	101
Figure 3.7: Bench-type tensile test machine for measuring membrane tensile strength.....	103
Figure. 4.1: The relationship and direction of water flux as a function of applied pressure in FO, PRO, RO and PAO for an ideal semipermeable membrane. Figure modified from (Lee et al. 1981b).	116
Figure 4.2: Schematic of the lab-scale experimental setup for PAO process.....	119
Figure 4.3: Variation of water flux in the FO/PAO processes (a) at different applied pressures under different DS-FS combinations (BW refers to 10 g/L NaCl solution) and (b) at different DS concentrations using BW as FS at an applied pressure of 6 bar. The data points refer to the experimental water flux while dotted lines refer to the theoretical flux calculated using models discussed under Section 2.	125
Figure 4.4: Influence of applied pressure on the water flux and the net gain in water flux under various DS concentrations for the three fertilisers used as DS using 10 g/L NaCl solution as FS. (a) For SOA, (b) for KCl, (c) for MAP and (d) the net gains in the water flux per unit applied pressure (specific water flux) when a hydraulic pressure of 10 bar was applied on the feed side of the membrane. In Figure 4.3 (b), the applied pressure of 6 bar was used since during the initial stage of the study, a lower applied pressure was preferred until it was realised later that higher applied pressure was possible and hence 10 bar was used in this experiment.	128
Figure 4.5: Variation of the water fluxes when the hydraulic pressure is applied under the condition in which the osmotic equilibrium occurs at different DS-FS concentrations levels (a) using three fertilisers as DS with BW as FS (with concentrations ranging from 0 to 35 g/L NaCl at an applied pressure of 10 bar and (b) using NaCl as DS with FS ranging from 0 to 35 g/L NaCl at an applied pressure of 6 bar and the variation of the effective osmotic pressures of the DS and FS at the	

membrane surface. The equivalent concentrations of SOA, KCl and MAP were determined using OLI Stream Analyser 3.2.	133
Figure 4.6: Influence of reverse diffusion of draw solutes and the feed solute rejection due to applied pressure in the PAFDO process.	136
Figure 4.7: Variations in the expected concentrations of the diluted SOA fertiliser DS with total membrane area in the PAFDO process under the hydraulic pressures of 10 and 20 bar applied at the osmotic equilibrium between diluted SOA DS (20.2 g/L) and 10 g/L NaCl FS. Simulations were performed for 8040 CTA FO membrane element with an effective membrane area of 9.0 m ² per element. Initial DS flow rate for 8040 CTA element was assumed at 120 L/h. For this particular simulation, influence of feed recovery rate was neglected for convenience and hence the results may slightly vary in the values although the trend would be similar. Readers are advised to consider the relative trend rather than the absolute data in this figure as more accurate simulation would require taking many other factors into considerations.	140
Figure 5.1: Chemical structure of PES and SPES synthesized in this study.....	148
Figure 5.2: PES sulphonation reaction and preparation procedure (Li et al. 2007).....	149
Figure 5.3: Polyamide formation by reaction between TMC and MPD (Tang. et al. 2009).	151
Figure 5.4: SEM images of membrane substrates with different blending ratio of sulphonated polymer for TFC fabrication: (a) no sulphonated polymer; (b) 25 wt % sulphonated material; (c) 50 wt% sulphonated material. All samples were fabricated through 12 wt% polymer concentration in NMP.	156
Figure 5.5: FTIR spectra of membrane substrate sample for PES and SPES 50 wt%.....	159
Figure 5.6: Performance comparison of fabricated membranes in terms of water flux and reverse solute flux under FO and PRO with various NaCl concentrations as DS and DI water as feed. (a) performance of membrane samples in terms of water flux, (b) performance of membrane samples in terms of reverse solute flux. (TFC ₁ contains 0 wt % sulphonated material in the membrane substrate while TFC ₂ and	

TFC ₃ have 25 wt % and 50 wt % sulphonated material in the membrane substrates respectively).	163
Figure 6.1: Schematic of RO and FO membrane fabrication methods in commercial scale. Modified from (Herron 2008).....	177
Figure 6.2: Picture and SEM images of membranes substrate displaying (a) T ₅ sample on backing fabric support casted through method 1 and (b) substrate caste without backing fabric (Both (a, b) fabricated from 18 wt % PES in 72 % NMP and 10% PEG solvent). Picture and SEM images of membranes substrate displaying (c) T ₅ sample cast on woven polyester mesh with 25% precent open area and (d) T ₁ sample cast on compacted woven polyester mesh with 5% precent open area (Both (c, d) fabricated from 18 wt % PES in 72 % NMP and 10% PEG solvent and casting method (1)).	186
Figure 6.3: SEM images of T ₁ membrane substrate displaying (a) cross-section and (b) bottom surface cast on compacted woven polyester mesh fabric support fabricated from 18 wt % PES in 72 % NMP and 10 % PEG solvent. This sample was fabricated through casting method 1.....	190
Figure 6.4: SEM images of T ₂ membrane substrate displaying (a) cross-section and (b) bottom surface cast on compacted woven polyester mesh fabric support fabricated from 18 wt % PES in 62 % NMP and 20 % PEG solvent. This sample was fabricated through casting method 1.	190
Figure 6.5: SEM images of T ₃ membrane substrate displaying (a) cross-section and (b) bottom surface cast on compacted woven polyester mesh fabric support fabricated from 12 wt % PES in 88 % NMP solvent, without PEG as pore former. This sample was fabricated through casting method 1 and backing fabric was not pre-treated with NMP solvent prior to casting.	191
Figure 6.6: SEM images of T ₄ membrane substrate displaying (left) cross-section and (right) bottom and surface cast on compacted woven polyester mesh fabric support fabricated from 18 wt % PES in 72 % NMP and 10 % PEG solvent. This sample was fabricated through casting method 2 (FO style on large scale).	191

Figure 6.7: SEM cross section images of Woongjin FO membrane substrate displaying (a) new membrane and (b) after few FO experiments. Woongjin membrane is a TFC-FO membrane cast on unknown nonwoven fabric support....193

Figure 6.8: SEM images of membrane substrate displaying (a) cross-section for T₃ sample on compacted woven polyester mesh fabric fabricated through casting method 1 and (b) bottom surface for T₄ sample cast on regular woven polyester mesh fabric fabricated through casting 2. Complete casting solution condition presented in Table 6.1.199

Figure 6.9: SEM images of membrane rejection thin layer displaying (a) top surface view for T₁ sample and (b) cross section view for T₂ sample cast on PES membrane substrate through interfacial polymerisation. Thin polyamide cross-linked rejection layer formed through reaction between 3.5 wt % MPD in water and 0.15 % TMC in hexane.203

Figure 6.10: Performance comparisons of fabricated membranes with commercial membranes in terms of water flux (a) with 0.5 M NaCl as DS and DI water as FS and (b) 0.5 M NaCl as DS and BW10 as FS at different applied hydraulic pressure.....205

Figure 6.11: Variation of water flux in the fabricated membrane with commercial membranes with 0.5 M NaCl as DS and DI water as FS at an applied pressure of 0 and 10 bar.208

Figure 6.12: Salt permeability versus water permeability for the synthesized TFC and commercial membranes.210

Figure 6.13: Influence of reverse salt flux due to applied pressure in the PAO process using 0.5M NaCl as draw solution and DI water as FS.211

LIST OF TABLES

Table 2.1 History of draw solutes used in FO with different regeneration methods. Modified from (Ge et al. 2013).	31
Table 2.2 Recent FO membranes made through phase inversion. DI water was used as the feed.	55
Table 2.3 Recent FO composite membranes. DI water was used as a feed.....	65
Table 4.1: Essential parameters used for mathematical modelling for FO and PAO processes.....	120
Table 5.1: TFC-FO casting solutions composition with different sulphonated polymer blending ratio.	150
Table 5.2: Characteristics of membrane substrates at different sulphonation rates..	157
Table 5.3: Mechanical properties of membranes with a different degree of sulphonation.	158
Table 5.4: Transport properties and structural parameters of fabricated membrane samples in comparison with CTA-HTI membrane.	162
Table 5.5: Performance of fabricated TFC-FO membrane using 2 M NaCl as DS and DI as FS under FO and PRO mode.	165
Table 5.6: Performance comparison of flat sheet TFC-FO membranes in FO mode of operation.	167
Table 6.1: Synthesis conditions for TFC PAO membranes.	175
Table 6.2: Characterisation of membrane substrates.	194
Table 6.3: Mechanical properties of TFC membrane substrates.	196
Table 6.4: Properties of fabricated TFC and other commercial membranes.....	201